AN OVERVIEW OF BIOMASS THERMOCHEMICAL LIQUEFACTION RESEARCH SPONSORED BY
THE U.S. DEPARTMENT OF ENERGY

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BACKGROUND

Biomass represents an important energy resource in the United States both at present and as a potential energy contributor for the future. In 1981, for example, it is estimated[1] that biomass contributed about 3.5% of the nations' energy supply, approximately equivalent with nuclear energy which contributed 3.8% in that year. With proper resource management and the development of efficient conversion processes, the Office of Technology Assessment has estimated[2] the potential contribution of biomass to the United States energy supply could range as high as 17 quadrillion Btu per year--almost 20% of current United States energy consumption. Similarly, the Energy Research Advisory Board (ERAB) has estimated[3] that biomass could potentially supply the nation with about 10 quadrillion Btu by the year 2000.

A wide variety of biomass resources such as wood and forest product residues, grasses, agricultural crops and their residues, and animal wastes can be used as energy feedstocks. As an abundant, renewable, domestic energy resource, biomass can help the United States reduce its dependence on imported oil and natural gas. Liquid fuels derived from biomass are expected to contribute significantly to the energy potential from this resource.

Liquid fuels from biomass offer several advantages over the biomass resource itself. Perhaps most important, liquid fuels have a higher energy density. The energy content of wood, for instance, is about 8500 Btu/lb, roughly half that of liquid hydrocarbon fuels. The effective bulk energy density of biomass solids on a volumetric basis is even lower if the void space between the solids is considered. A cubic foot of dry wood chips for instance, has an energy content of about 90,000 Btu. This is less than one-tenth the energy density of gasoline which contains about 928,000 Btu/ft^3. The higher energy density of liquid fuels from biomass allows the products to be transported more economically and to be more easily stored. Liquid fuels also match existing end-use patterns, particularly in the transportation sector. Biomass is the only renewable energy technology capable of addressing this need for transportation fuels.[4]

Thermochemical conversion processes offer promising methods for converting biomass to gasoline-compatible liquid fuels. Thermochemical conversion processes employ elevated temperatures to convert the biomass feedstock. Thermal conversion processes are well suited to conversion of wood and crop residues which account for about 96% of the biomass resources in the United States.[2] These processes can convert 85 to 95% of the organic material in such feedstocks with little sensitivity to variations in the feed material.

Biomass direct liquefaction process are those which produce liquids as primary initial products, usually at moderate temperatures (250 to 600°C). Pyrolytic and catalytic liquefaction processes which produce biocrude oils are examples. The biocrude oils would be suitable for some uses as produced or for upgrading into gasoline-compatible fuels. As will be described in greater detail later, the biocrude oils are quite different chemically than petroleum crude oils, and different refining and upgrading procedures are necessary. Indirect liquefaction processes,

by comparison, first convert the biomass to simple gaseous components including H_2 and CO and then synthesize these into liquid products. Methanol production is an example. Mechanical extraction of natural products from various biomass species followed by limited thermal or physical treatment can also supply liquid fuels. Various seed oils, for instance, have been used as extenders for diesel fuels.

In this paper we present an overview of biomass direct liquefaction research being sponsored by the U.S. Department of Energy's Biomass Thermochemical Conversion Program. Pacific Northwest Laboratory provides field management for this program as shown in Figure 1.

BIOMASS DIRECT LIQUEFACTION RESEARCH

Liquid fuels research sponsored by the Thermochemical Conversion Program focuses on biomass direct liquefaction processes capable of producing true hydrocarbon fuels. This is achieved by first converting the biomass feedstock to a biocrude product using various liquefaction processes. The crude oils produced in these processes are subsequently upgraded into true hydrocarbon products. The ability to generate true hydrocarbon fuels is very important to ensure compatibility with existing gasoline based fuels and fuel distribution systems. Thermochemical conversion processes are necessary for producing true hydrocarbons from biomass.
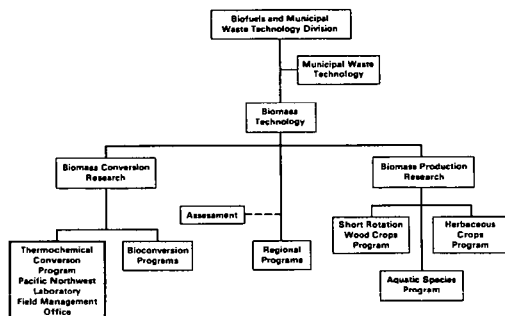

Fig. 1 - Organization of the Biomass Thermochemical
Conversion Program

Projects being funded by the Biomass Thermochemical Conversion Program are shown in Figure 3. The research is directed at exploring of methods for generating biocrude liquids and at upgrading them into high value hydrocarbon fuels.

PRODUCTION OF BIOCRUDE LIQUIDS

The initial step in the conversion of biomass to hydrocarbon fuels is the production of an intermediate biocrude liquid. This step can be accomplished using several different approaches. These are discussed below.

PYROLYTIC LIQUEFACTION - Pyrolysis refers to the heating of biomass in the absence of air. Traditionally, pyrolysis has been used to produce charcoal. Conventional pyrolysis typically produces about one-third each gases, pyrolysis oils, and char. The process is inefficient because large quantities of low-value liquids and gases are formed in addition to desired solid products. Batchwise, often primitive, conversion units have also added to the inefficiency of conventional pyrolysis processes.

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In recent years, the concept of rapid pyrolysis has emerged as a promising alternative for producing liquid fuels. By carefully controlling both the heating rate and the temperature, the yields of liquid biocrude products can be increased to over 65% by weight on a moisture, ash-free basis.[5] Under some conditions, up to about 20% high value olefinic products can be produced.[6]

Georgia Tech Research Corporation, Atlanta, Georgia, is conducting research on rapid pyrolysis of biomass with the goal of producing low cost liquid products. The research makes use of an entrained flow pyrolyzer where biomass is converted primarily to liquid products under conditions of moderate heating rates and temperatures. The system, as shown schematically in Figure 3, consists of an entrained, upflow reactor and an oil recovery system that allows partial on-stream fractionation of the product. Georgia Tech Research Corporation has established the interdependence of the reaction temperature and residence time on pyrolysis oil yield. Testing over temperatures from 400 to 550°C gave mass yields of moisture-free oil ranging from 31 to 53%. Additional testing should complete parameter optimization studies.
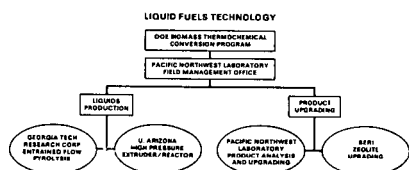

Fig. 2 - Liquid Fuels Projects
          Sponsored by the Thermo-
          chemical Conversion Program
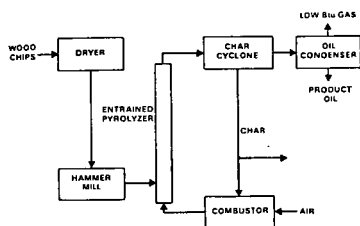
Fig. 3 - Schematic Diagram of
          Entrained-Flow Pyrolysis
          Reactor at Georgia Tech Research
          Corporation

CATALYTIC LIQUEFACTION - Catalytic direct liquefaction research, at this time, is based on a concept first proposed by the Pittsburgh Energy Research Center. In this concept, biomass is mixed with recycled wood oil and sodium carbonate catalyst along with a H_2/CO reducing gas. The mixture is injected into a high-pressure vessel (3000 psi) and heated to about 350°C. The product stream is cooled and flashed into a pressure let-down vessel. The oil phase product is withdrawn and part of it is recycled for use as slurry medium.

In 1980 and 1981, this process and an aqueous slurry version, proposed by Lawrence Berkeley Laboratory, were tested in a DOE research facility located at Albany, Oregon. This research showed the technical feasibility of producing biomass derived liquids by both the oil slurry and aqueous slurry process variations. In one test run during 1981, over 11,000 lbs of direct liquefaction oils were produced during operation in the oil slurry mode. The tests, however, also showed the need to reduce the large oil recycle requirement in order to improve process economics. The Thermochemical Conversion Program is attempting to improve the competitiveness of direct liquefaction through the use of increased feedstock slurry concentrations.

The University of Arizona, Tucson, Arizona, is conducting research on an advanced concept for direct liquefaction that would use very concentrated biomass slurries. The goal of this work has been to use a polymer extruder as a slurry feeding/pumping device. The modified extruder/feeder system is capable of handling slurries as concentrated as 60% wood solids in biomass oil. Conventional systems, by comparison, typically cannot handle slurries containing over about 20% wood. The University of Arizona had designed and constructed and integrated extruder/static mixer liquefaction system as shown in Figure 4. The static mixer is expected to allow adequate mixing and agitation of the viscous slurries.
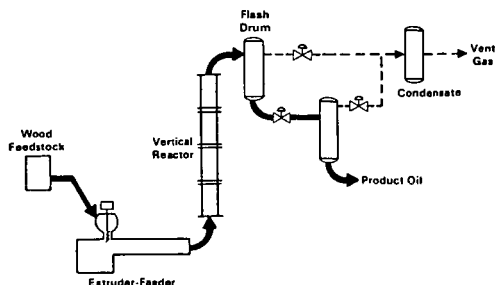
Fig. 4 - Schematic Diagram of Catalytic Liquefaction
Unit at the University of Arizona

The University of Arizona has completed construction of the research unit and has began experimental operation. Results to date show that the unit can be operated consistently and reliably over a variety of experimental conditions. The biocrude product produced is low in oxygen content and has a high heating value. Properties of the oil are summarized in Table 1.

Table 1 - Properties of Crude Oil from the Wood
Produced by the University of Arizona
(Dry Basis)

Elemental Analysis:

C	83.4%
H	7.9%
0	8.5%
Heating Value (HHV)	16,000 Btu/lb

During 1987, the University of Arizona will operate the experimental unit to determine the effect of lowering or eliminating both the carbonate catalyst and the reducing gas. Preliminary results show that the reactor can operate when those two additives are eliminated, but the effect on product quality has not yet been determined.

PRODUCT CHARACTERIZATION AND UPGRADING

In addition to research on liquefaction concepts, the Thermochemical Conversion Program is also sponsoring research on the characterization of the biocrude products and their subsequent upgrading into gasoline compatible hydrocarbon fuels. This research is described below.

Pacific Northwest Laboratory, Richland, Washington, is conducting research on the characterization and upgrading of both pyrolytic and catalytic liquefaction oils. Characterization studies indicate that there are significant differences between the pyrolytic and the catalytic liquefaction oils. As shown in Table 2, pyrolysis oils contain more oxygen and are less viscous than the catalytic liquefaction products. The catalytic liquefaction products contain large quantities of phenolic compounds while the pyrolysis oils have large concentrations of organic acids. These differences directly impact the methods for upgrading these products.

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Table 2 - Biomass Liquefaction Products Comparative
Analytical Data

	Catalytic Liquefaction Oil (PERC-Albany TR12)	Pyrolysis Oil (Georgia Tech #11)
Elemental Analysis (MAF)		
Carbon	81.0%	59.2%
Hydrogen	10.2%	7.0%
Oxygen	8.8%	33.8%
Nitrogen	0.1%	0.1%
Sulfur	1.5%	1.4%
Moisture and Heating Value		
% H_2O	7.3	19.7
raw HHV	14,200 Btu/lb	7,950 Btu/lb
MAF HHV	15,300 Btu/lb	9,800 Btu/lb
Other Properties		
viscosity cps @ 40°C	400,000	62
density g/ml @ 23°C	1.14	1.24
pourpoint	27°C	-15°C

Research at PNL has concentrated on upgrading the biocrude liquids to gasoline-like motor fuels. This research uses nickel/molybdenum and cobalt/molybdenum catalysts in a continuously fed, bench-scale reactor to hydrotreat the liquefaction crude oils. Initial research has focused on the catalytic liquefaction oils due to their lower initial oxygen content and higher stability. Hydrotreating under conditions of 350 to 400°C at pressures of 2000 psi selectively eliminates oxygen and yields primarily hydrocarbon materials. Comparisons of key constituents and of relative properties of the crude and upgraded products are shown in Tables 3 and 4. Research indicates that the octane number for the hydrocarbon product is about the same as straight run gasoline from petroleum sources.

Table 3 - Comparison of Typical Constituents of
Biomass Catalytic Liquefaction Biocrude
Oil and Hydrotreated Product (Albany TR-7
Oil)

Biomass Crude Product	Refined Biomass Oil
Cyclic Keytones	Cyclohexane
Unsaturated Cyclic Keytones	Alkyl-Cyclohexanes (to C-10)
Alkyl-Phenols	Benzene
Methoxy-Phenols	Toluene
Di-Phenols	Xylene
Napthols	Other Alkyl-Benzenes

Table 4 - Comparison of Properties of Biocrude Oils
and Hydrotreated Product (Albany TR-7 Oil)

	Biocrude Oil	Refined Biomass Oil
Hydrogen to Carbon Ratio	1.21	1.61
Oxygen Content (%, MAF Basis)	11	0.3
Density (g/cm^3)	1.19	0.83
Viscosity (cPs @35°C)	100,000	1.1
Heating Value (HHV, MAF Basis)	15,800	18,900

Pacific Northwest Laboratory also initiated research on the upgrading of the pyrolytic liquefaction oils. The pyrolytic oils are expected to be less expensive to produce but more difficult to upgrade due to their higher oxygen content and lower stability. The lower stability of the oil results in extensive char formation and reactor plugging when the pyrolysis oils are hydrotreated under conditions similar to the catalytic liquefaction products. Preliminary research has indicated that a two-step process may be feasible for upgrading the pyrolysis oils. The initial step would use a mild treatment with a nickel catalyst at relatively low temperature (260 to 280°C) followed by a second hydrotreating step similar to that use with the catalytic liquefaction products. Additional research on this concept will be conducted in FY86.

Solar Energy Research Institute (SERI), Golden, Colorado, is also conducting research on the upgrading of biomass pyrolytic liquefaction oils. The concept being explored uses zeolite catalysts to convert the pyrolysis oils to hydrocarbon fuels. The pyrolysis oil vapors would be reacted on the catalyst directly downstream from the pyrolysis reactor, eliminating the need for intermediate condensation of the pyrolytic products. The zeolite catalysts could also eliminate the need for hydrogen in the upgrading process. The zeolite catalysts are known to produce gasoline-like hydrocarbons from a variety of oxygenated feedstocks such as methanol.

Preliminary studies at SERI using mass spectroscopic techniques showed that zeolite catalysts are reactive with respect to the biomass tars and will produce hydrocarbon products. During 1986, SERI completed modification of their ablative pyrolysis reactor to include a slipstream reactor so the pyrolytic vapors could be directly upgraded. Using a zeolite catalyst donated by Mobil Corporation, SERI has now shown that the catalyst can effectively deoxygenate biomass vapors to produce hydrocarbons. In 1987, research is continuing to determine catalyst lifetimes, the extend of carbon deposition, and related factors in order to optimize reaction conditions.

ADDITIONAL INFORMATION

Detailed descriptions of all the research and development projects funded by the Biomass Thermochemical Conversion Program are given in the Proceedings of the 1985 Biomass Thermochemical Conversion Contractors' Meeting, October 1985. This document, PNL-SA-13571/CONF-8510167, is available from the National Technical Information Service, United States Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.

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CATALYST SPECIFICITIES IN HIGH PRESSURE HYDROPROCESSING
OF PYROLYSIS AND GASIFICATION TARS

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ABSTRACT

Over a period of several years [1], the Department of Forest Science at Texas A&M
University has been conducting studies in the hydroprocessing (catalytic high pressure
hydrotreating or hydrodeoxygenation accompanied by hydrocracking) of pyrolytic tars
produced in biomass pyrolysis and gasification. Upgrading through hydroprocessing
results in good yields of volatile hydrocarbon and phenolic products. This paper
compares the performance of twenty different catalysts selected for hydroprocessing of a
pine pyrolysis oil, describes the use of noble metal catalysts with tars produced from
nine different biomass feedstocks (oil from pine pyrolysis and the tars from pine wood
chip, pine plywood trim, pecan shell, peanut shell, sugarcane bagasse, corncob, rice
hull, and cottonseed hull gasification), and compares the use of several catalysts in a
trickle bed reactor for kinetic studies of the hydroprocessing reaction.

METHODOLOGY

Feedstock and Materials. Pine pyrolytic oil produced by Tech-Air Corporation form
sawdust and bark in the Cordele GA demonstration plant was used as the base oil in this
study. A barrel of this oil was generously provided by American Can Company. Other
tars from agricultural residues were produced in a modified gasification-pyrolysis
reactor (100 kg capacity updraft gasifier run under conditions to promote tar
production).

Catalysts used for the batch reactor studies were used in the form purchased from
Strem, Harshaw, or donated by UOP (Table 1). For the trickle bed reactor studies, the 5%
Pt/Al₂O₃ powder catalyst was mixed with Ludox AS-40 binder in proportions that the final
catalysts contained 30% SiO₂. A paste was made when the binder was added, and this
paste was taken up into a syringe with a 1/16 inch plunger. The catalysts was extruded,
dried and calcined in air at 756°K (483°C) for four hours. In order to obtain an active
catalyst, the Pt/Al₂O₃ pellet was reduced *in situ* prior to the experiments. The
reduction was done by passing H₂ through the catalytic bed at 673°K, 8270kPa at a flow
rate of 200 cm³/min (21.1°C, 1 atm) for one hour.

For Harshaw's catalysts, the sulfided form was used. Presulfiding of the catalysts
was done *in situ* prior to the experiments. A mixture of 90% H₂ and 10% H₂S by volume
was passed through the catalyst bed at a flow rate of 40 cm³/min (measured at 21.2°C, 1
atm) at 673°K and atmospheric pressure until the outlet gas showed no further sign of
H₂S consumption.

Decahydronaphthalene (decalin) purchased in purified grade from Fisher Scientific and
methyl cyclohexane produced by hydrogenation of toluene were used as hydrogen-donor
solvents in the hydroprocessing reactions.

Batch Reactor Studies. Some twenty catalysts (Table I) were used in preliminary
screening studies [2,3]. A number of experiments were conducted using the various
catalysts at differing reaction conditions in attempts towards optimization for each
catalyst, but the results obtained could not be tabulated to effect some ranking order.
Standard conditions chosen were those found to be effective for the 5% Pd and 5% Pt
catalysts in the preliminary study - 60g stripped pine pyrolytic tar (water removed
through azeotropic distillation with toluene), 100g solvent (decalin or methyl
cyclohexane), 20g catalyst, 1000 psi (@ ambient temp.) hydrogen feed and 400°C for 60

minutes in a rocking reactor (Aminco 4 3/8 inch o.d. series, 1500 ml capacity, rated at 5500 psi). After the reactions, the following were calculated (Tables II and III): *hydrocarbon conversion %* (total liquid product corrected for solvent and water concentrations), *water yield %* (water produced as % of pyrolytic tar feed – a measure of hydrotreating or hydrodeoxygenation activity), *gases and losses %* (balance of products by difference as % of pyrolytic tar feed – a measure of excess hydrocracking activity in the production of gaseous hydrocarbons). For a few catalysts with limited catalytic activity, a fourth component of the reaction product was calculated: *tar residue %*. Tar residue is the heavy tar deposited on catalysts and insoluble in the reaction solvent selected (determined by weighing dirtied catalyst after reaction, subtracting weight of catalyst used, and expressing as % of pyrolytic tar feed).

Trickle-bed Reactor Studies. A schematic for the trickle-bed reactor system is shown in Figure 1 [4,5]. The reactor proper consists of a 32-inch long 316 SS tube, 3/4 inch O.D., 0.065 inch thick. The bottom 12 inches contained an inert support, Pyrox 3 mm dia. glass beads, with the top 20 inches packed with catalyst. The reaction temperature was non-isothermal, *viz.* 22 inches of the reactor was immersed in a salt bath (Hotec heat transfer salt, a mixture of 53% potassium nitrate, 40% sodium nitrite, 7% sodium nitrate; air bubbled through bath to ensure uniform temperature profile), so that the salt around the bottom half of the catalyst bed (10 in) was at temperature, while the temperature of non-immersed top half decreased linearly from near reaction temperature at the top of the salt bath to 190°C at the top of the reactor. By using non-isothermal conditions, the temperature inside the reactor increased gradually along the reactor length, preventing the volatiles in the pine pyrolysis oil from flashing into the gas phase suddenly. With the catalyst packed at the top of the reactor, the pyrolysis oil was hydrotreated before the oxygen-containing compounds could polymerize at high temperature. The NiW catalyst is a strong cracking catalyst and was thus not effective in hydrotreating: oxygen-containing components in the oil polymerized in the reactor.

Under typical operating conditions, H_2 feed was 100 cc/min (at 60°C, 1 atm) per gram of pine pyrolysis oil input; liquid feed was used at a ratio of 2 grams decalin per gram of pine pyrolysis oil; weight hourly space velocity (g oil input per hr / g catalyst in the reactor) was 0.5 to 3.0 hr^{-1}; salt bath temperature was 673 to 673°K; H_2 pressure was 5272 to 10443 kPa (750 to 1500 psig); and, catalyst bed was 60 g. for each load. After the reaction, the catalyst was regenerated by burning in air to remove coke deposited on the catalyst during the reaction, then reactivated for the next run.

Sample and Product Chemical Analyses. Analytical techniques used to determine the chemical composition of raw oils and hydroprocessed products are given elsewhere in this volume [6].

RESULTS AND DISCUSSION

Batch Reactor Studies. Results for the 20 catalysts using the batch rocking reactor using decalin as hydrogen-donor solvent are given in Table II; those for the methyl cyclohexane solvent system in Table III. The 5% noble metal catalysts in both solvent systems generally gave superior results in hydrocarbon conversion and water yield. Note that hydrocarbon conversion efficiencies may appear low because these are expressed on a mass and not energy basis. With 27% oxygen content in the raw pyrolytic tar feed, maximum hydrocarbon conversion is 73% plus hydrogen uptake; maximum water yield is 30% (27 X 18/16). These data will be discussed in the oral presentation.

Trickle-bed Reactor Studies – Oxygen Removal. The effect of reaction temperature, pressure and space velocity on oxygen removal (hydrotreating, hydrodeoxygenation) are shown in Figures 2 through 4. The points in the figures are the experimental data and the solid lines were evaluated by using an oxygen removal model. A clear trend is observed for the effect of reaction temperature and pressure, while changes in space velocities did not affect oxygen removal. The Pt/Al₂O₃ catalyst exhibits the best activity for oxygen removal for pine pyrolysis oil among the four catalysts tested. The NiW catalyst was not effective in oxygen removal, and was dropped from further consideration.

Trickle-bed Reactor Studies - Kinetic Modeling. The proposed kinetic model for
hydroprocessing pyrolysis oil consists of the kinetic scheme as shown in Figure 5.
Terms used in this and subsequent figures are defined as follows (see other paper in
this volume [6] for examples of the GPC chromatograms):

heavy nonvolatiles - nonvolatiles in GPC fractions 1 and 2.
light nonvolatiles - nonvolatiles in GPC fractions 3 and 4
phenols   - volatiles in GPC fraction 3 detectable by GC
aromatics   - volatiles in GPC fractions 4 and 5, excluding solvents
alkanes   - volatiles in GPC fraction 2
coke + H$_2$O +   - 1 minus liquid yield
   outlet gases
liquid yield   - (wt. of fractions by GPC) - (solvents in hydroprocessed oil)
                                 pine pyrolysis oil input

An elaboration of the kinetic model is outside the scope of this preprint. The
outcome, expressed as experimental and predicted values of the lumped species in the
kinetic model at various reaction conditions (temperature, pressure and space velocity
effects) is presented in Figures 6 through 14.

Effect of Reaction Temperature (Figures 6 to 8). Temperatures selected for study were
623, 648 and 673°K. All reactions were run at 8720 kPa and WHSV 2 hr^{-1}.

Effect of Reaction Pressure (Figures 9 to 11). The effect of reaction pressure was
evaluated at 5272, 6996, 8720 and 10443 kPa at 673°K and WHSV 2 hr^{-1}.

Effect of Space Velocity (Figures 12 to 14). WHSV was evaluated at 0.5, 1.0, 2.0 and
3.0 hr^{-1}. Pressure used was 8721 kPa; temperature, 673°K.

Results are essentially self-evident in these figures, but will be discussed in detail
in the oral version and final manuscript of this communication.

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TABLE I.	CATALYSTS SCREENED FOR HYDROTREATING AND HYDROCRACKING OF BIOMASS THERMOCHEMICAL TARS		
5% Pd/alumina	2% Pt/alumina	0.5% Pd/alumina	
5% Pd/carbon	5% Pt/alumina	0.5% Pt/alumina	
	5% Pt/carbon	0.5% Re/alumina	
5% Re/alumina			
5% Rh/alumina	Harshaw CoMo-0603	silicated gamma alumina	
5% Ru/alumina	Harshaw HT-400	NiO-WO$_3$ /silica alumina	
	Harshaw Ni-4301		
Raney Ni		UOP Lomax	
NiCO$_3$	ZrO$_2$ on alumina	UOP Unibon	

BPR : Back Pressure Regulator
C   : Cooling
F   : Filter
G   : Gas Sample collector
L   : Liquid Sample Collector
MF : Mass Flow Meter
P   : Pressure Guage
R   : Regulator
TC : Temperature Controller
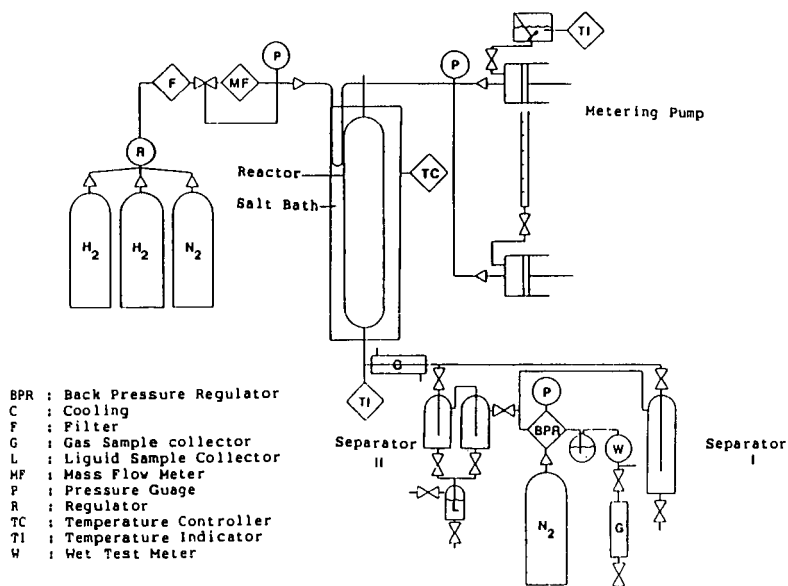TI : Temperature Indicator
W   : Wet Test Meter

Figure 1. Schematic process of trickle-bed reactor system

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TABLE II. HYDROPROCESSING OF TECH-AIR PINE PYROLYSIS OIL IN DECALIN SOLVENT[1]

Catalyst Type	Hydrocarbon Conversion[2] %	Water Yield[2] %	Tar Residue[2] %	Gases & Losses[2] %
5% Pd/alumina	55.7	25.3	–	19.0
5% Pd/carbon	35.7	21.7	–	42.5
5% Pt/alumina	44.5	24.5	–	31.0
5% Pt/carbon	33.1	17.7	–	49.2
5% Rh/alumina	39.3	15.8	–	44.8
5% Ru/alumina	25.8	20.0	–	54.2
5% Re/alumina	44.3	18.2	–	37.5
UOP Lomax	43.5	8.3	–	48.2
UOP Unibon	33.3	6.6	–	60.1
Raney Ni	40.1	19.6	–	40.3
2% Pt/alumina	51.4	5.0	–	43.6
0.5% Pd/alumina	18.4	9.8	–	71.2
0.5% Pt/alumina	25.7	10.8	–	63.5
0.5% Re/alumina[3]	–	10.1	75.4	–
Ni-4301	11.9	8.3	40.3	39.5
CoMo-0603	4.2	6.0	41.2	48.6
HT-400	3.4	7.5	57.9	31.2
ZrO$_2$	25.1	7.4	35.9	31.6
silica alumina	3.3	13.2	69.9	13.6
silicated gamma alumina	11.4	6.7	45.3	36.6

[1] conditions as described in text
[2] defined in text
[3] hydrocarbon conversion very small; gases and losses % could not be calculated

TABLE III. HYDROPROCESSING OF TECH-AIR PINE PYROLYSIS OIL IN METHYL CYCLOHEXANE SOLVENT[1]

Catalyst Type	Hydrocarbon Conversion[2] %	Water Yield[2] %	Tar Residue[2] %	Gases & Losses[2] %
5% Pd/alumina	54.5	8.9	–	36.6
5% Pd/carbon	37.4	8.2	–	54.5
5% Pt/alumina	44.2	5.0	–	50.8
5% Pt/carbon	19.1	6.7	–	76.5
5% Rh/alumina	38.9	16.6	–	44.5
5% Ru/alumina	24.9	12.4	–	62.8
5% Re/alumina	37.1	20.0	–	42.8
UOP Lomax	38.0	5.0	–	57.0
UOP Unibon	35.6	7.5	–	56.9
Raney Ni	40.1	19.1	–	40.1
2% Pt/alumina	21.3	2.4	–	76.3
0.5% Pd/alumina	53.9	8.9	–	37.2
0.5% Pt/alumina	46.5	10.1	–	43.3
0.5% Re/alumina[3]	–	5.0	69.3	–
Ni-4301[3]	–	10.0	50.2	–
CoMo-0603[3]	–	4.8	46.6	–
HT-400[3]	–	8.3	60.6	–
ZrO$_2$[3]	–	5.0	63.4	–
silica alumina[3]	–	12.4	74.0	–
silicated gamma alumina[3]	–	1.7	61.7	–

[1] conditions as described in text
[2] defined in text
[3] hydrocarbon conversion very small; gases and losses % could not be calculated

TABLE IV. PROPERTIES OF RAW AND HYDROPROCESSED[1] BIOMASS PYROLYTIC TARS

RAW TARS

	Tech-Air	Wood Chips	Pecan Shell	Sugarcane Bagasse	Peanut Shell	Corncob	Rice Hull	Cotton Hull	Plywood Trim
Elem. Anal.[2] wt %:									
C	65.79	54.34	68.37	55.94	60.89	58.34	64.62	67.91	74.08
H	7.13	6.31	5.70	7.00	7.21	6.32	6.66	7.47	9.10
O	27.08	39.18	25.32	36.75	28.87	34.30	25.28	23.02	16.49
N	–	0.14	0.61	0.31	3.03	1.04	3.44	1.60	0.33
Heat Content MJ/kg	23.18	24.32	23.93	22.39	27.65	24.88	24.26	23.86	24.61
Spec. Gravity[2]	1.14	1.22	1.11	1.15	1.10	1.26	–	–	1.10
Ash Content[2] %	1.03	0.22	0.20	0.57	0.77	1.32	0.68	3.16	0.12
Water Content %	10.0	6.4	13.0	19.6	15.0	3.1	5.0	5.0	10.6

HYDROPROCESSED[1] TARS

	Tech-Air	Wood Chips	Pecan Shell	Sugarcane Bagasse	Peanut Shell	Corncob	Rice Hull	Cotton Hull	Plywood Trim
Elem. Anal.[2] wt %:									
C	83.20	79.48	81.58	78.62	78.50	83.40	81.78	82.05	81.14
H	12.70	9.79	10.96	9.26	9.85	9.22	10.53	10.80	9.51
O	14.10	10.57	6.41	11.25	10.24	5.49	5.53	5.53	8.45
N	–	0.26	1.06	0.75	1.41	1.89	2.16	1.38	0.90
Heat Content[2] MJ/kg	40.26	38.19	40.24	38.15	38.33	39.32	37.37	41.02	38.91
Spec. Gravity[2]	0.87	0.90	0.90	0.94	0.95	0.88	0.93	0.90	0.89
Conversion[3]									
wt %	71.7	58.1	67.3	57.7	74.7	58.8	63.4	64.7	59.2
energy %	111.9	85.5	98.4	78.7	87.7	90.1	92.7	105.7	83.7

1 conditions used: 15g 5% Pd/alumina catalyst, 100g decalin, 400 C, 60 minutes, 6900 kPa H2
2 not corrected for moisture
  conversion, wt %, is (wt of product minus wt of solvent) over tar dry weight, times 100.
  conversion, energy %, is wt % times heat content of product over heat content of raw tar.

TABLE V.	SPECIFICATIONS FOR THE CATALYSTS USED IN THE TRICKLE BED REACTOR STUDY[1]			
Catalyst Type	Pt/Al_2O_3	CoMo	NiMo	NiW
Manufacturer	Strem 78-166	Harshaw HT-400	Harshaw HT-500	Harshaw Ni-4301
Size	powder	1/16" E.[2]	1/16" E.[2]	1/16" E.[2]
Composition	5% Pt	3% CoO, 15% MoO$_3$	3.5% NiO, 15.5% MoO$_3$	6% Ni, 19% W
Surface Area, m^2/g	100[3]	200	200	230
Pore Volume, cc/g	0.52[3]	0.45	0.46	0.37
Pore Size, dia, A	100	94	88	104

[1] conditions as described in text
[2] E. = extrudate
[3] for the pellet catalyst
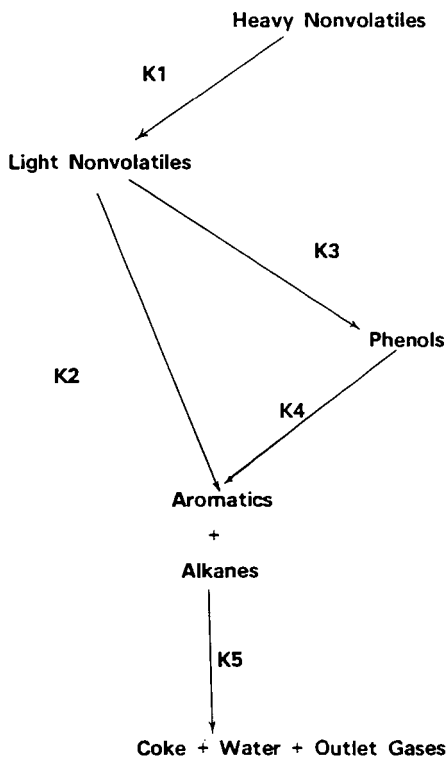
FIGURE 5.
Lumped Kinetic Scheme

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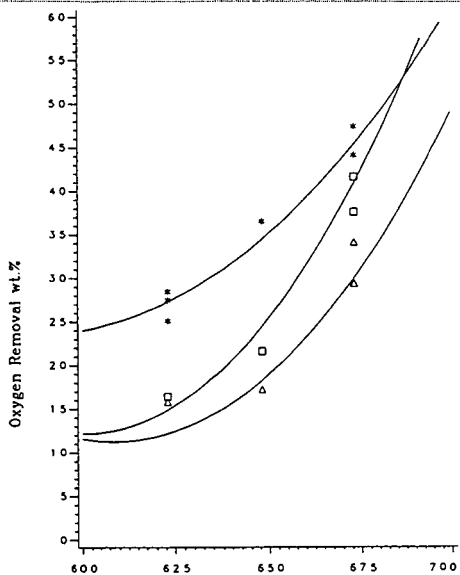
FIGURE 2 - Reaction Temperature, K
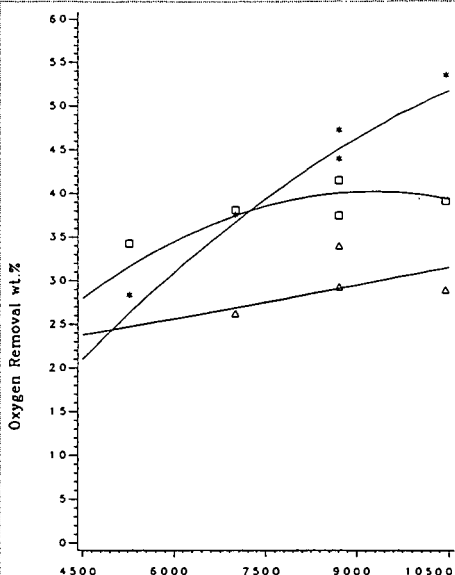
FIGURE 3 - Reaction Pressure, kPa
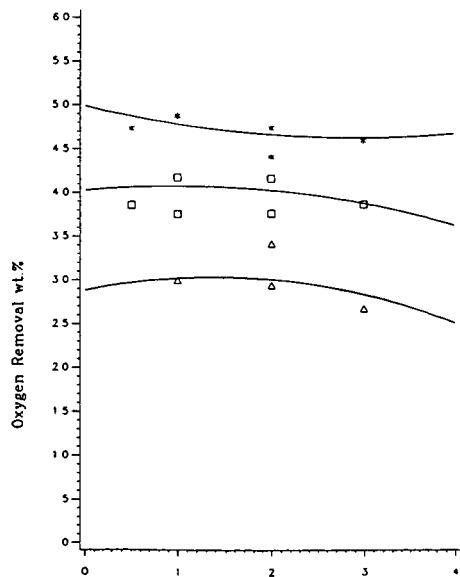
FIGURE 4 - Space Velocity, hr^{-1}

Effects of Reaction Temperature,
Reaction Pressure and Space
Velocity on Oxygen Removal -
Trickle-Bed Reactor Study

*   Pt catalyst

□   CoMo

△   NiMo

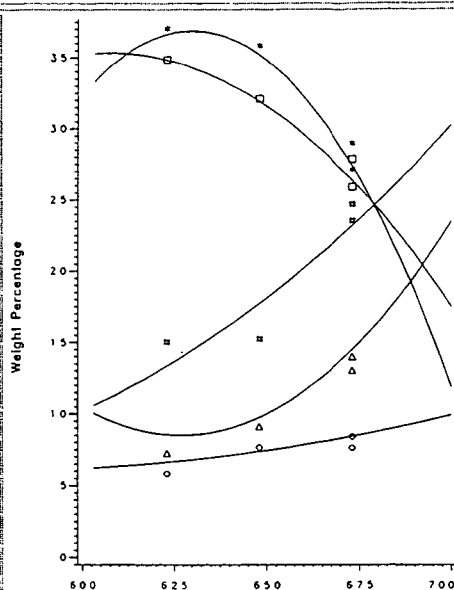—   Model Predictions
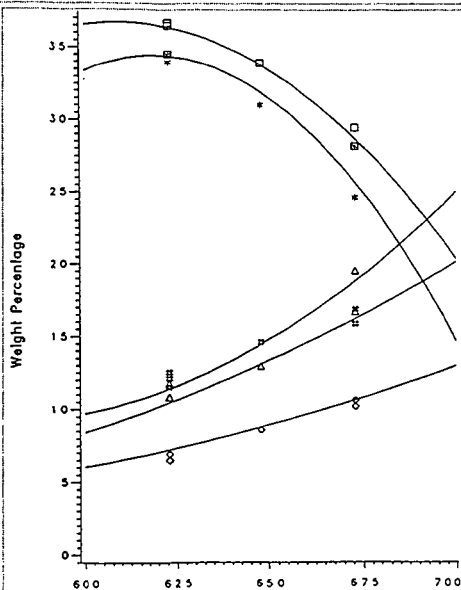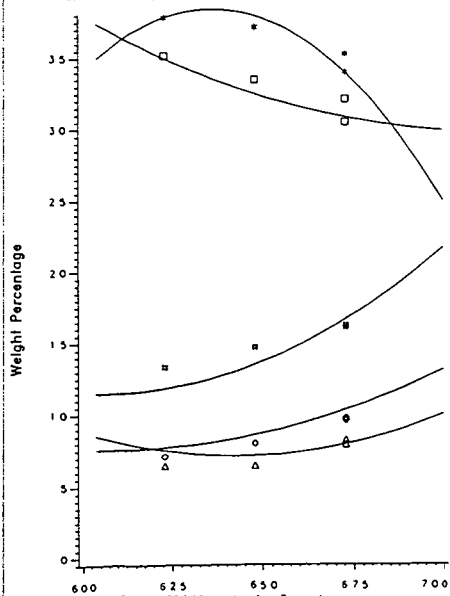
FIGURE 6 - Pt/Al₂O₃ Catalyst.

FIGURE 7 - CoMo Catalyst

FIGURE 8 - NiMo Catalyst

Effects of Reaction Temperature,
K, on Hydroprocessing -
8720 kPa, WHSV 2 hr⁻¹
Trickle-Bed Reactor Study

*   Heavy Nonvolatiles

▫   Light Nonvolatiles

○   Phenols

△   Aromatics + Alkanes
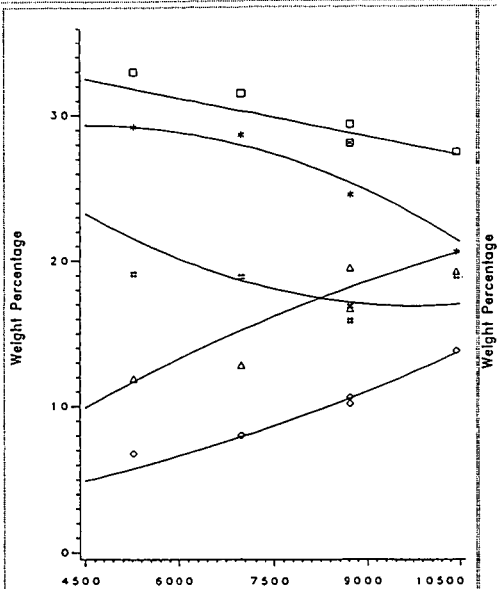
⌗   Coke + Water + Outlet Gases

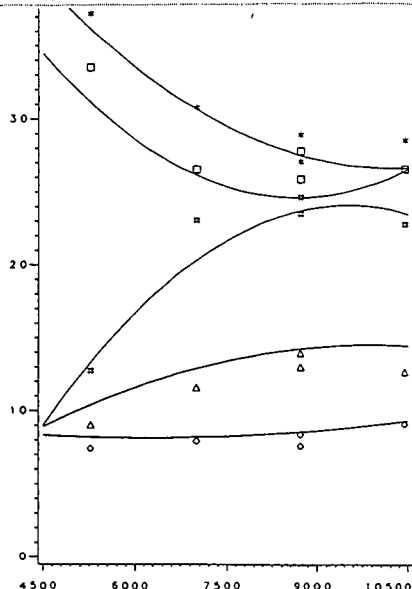——   Model Predictions

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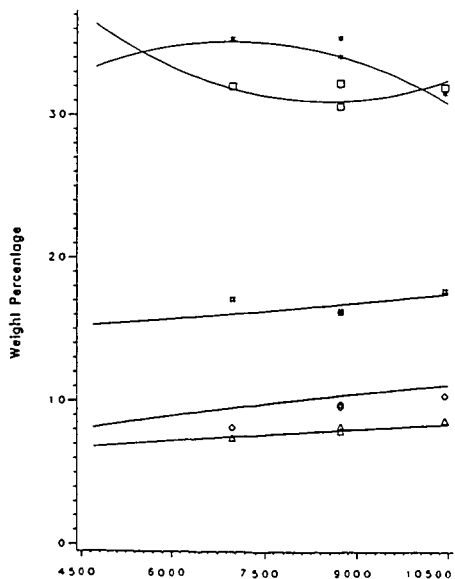FIGURE 9 - Pt/Al₂O₃ Catalyst

FIGURE 10 - CoMo Catalyst

FIGURE 11 - NiMo Catalyst

Effects of Reaction Pressure, kPa, on Hydroprocessing – 673 K, WHSV 2 hr^{-1} Trickle-Bed Reactor Study

*   Heavy Nonvolatiles
□   Light Nonvolatiles
○   Phenols
△   Aromatics + Alkones
⌗   Coke + Water + Outlet Gases
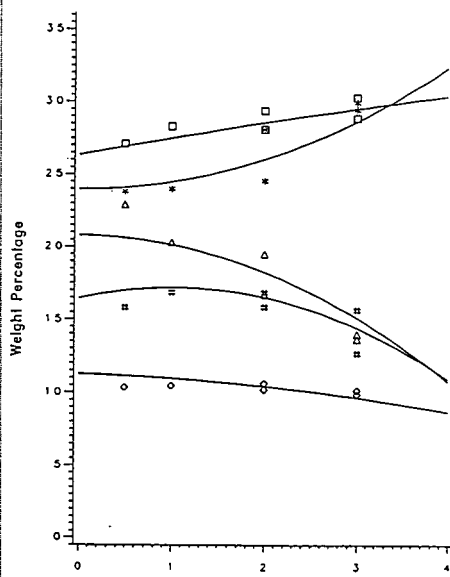——   Model Predictions
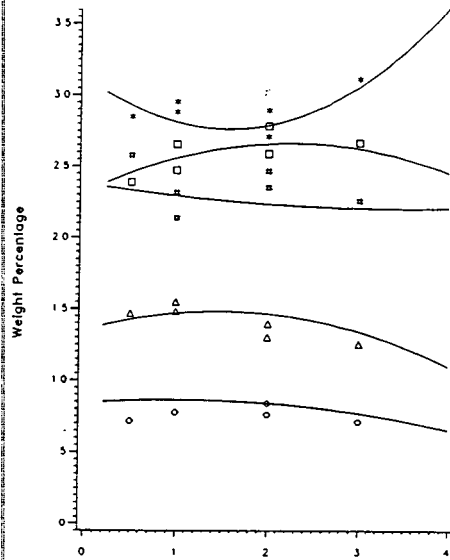
238

FIGURE 12 - Pt/Al₂O₃ Catalyst
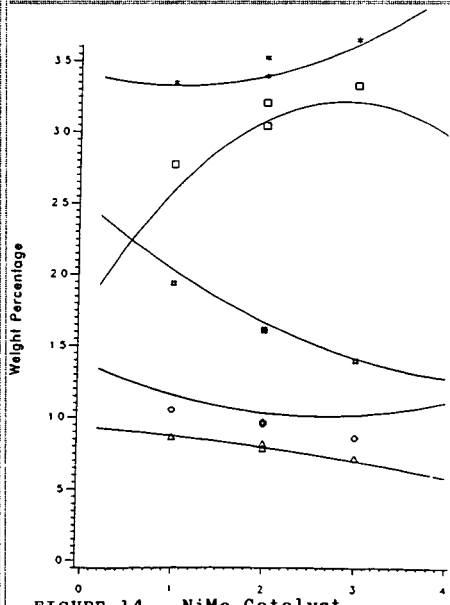
FIGURE 13 - CoMo Catalyst

FIGURE 14 - NiMo Catalyst

Effects of Space Velocity,
hr⁻¹, on Hydroprocessing –
8720 kPa, 673 K
Trickle-Bed Reactor Study

• Heavy Nonvolatiles

▢ Light Nonvolatiles

○ Phenols

△ Aromatics + Alkanes

✳ Cake + Water + Outlet Gases

— Model Predictions

CHEMICAL AND STOCHASTIC MODELING OF LIGNIN HYDRODEOXYGENATION

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Abstract

An *a priori* Monte Carlo simulation of the product spectrum resulting from the thermal and catalytic depolymerization of lignin has been developed. The simulation combines model compound reaction pathways and kinetics, deactivation parameters, and stochastic models of polymer diffusion into a Markov-chain based simulation of the reaction of lignin polymers. Predicted product class ratios of single-ring phenolics were in reasonable agreement with experimental data pertaining to lignin liquefaction, especially as regards neat pyrolysis. The advantage of catalytic liquefaction was suggested by the increase in single-ring product yields, especially those of phenols and hydrocarbons, relative to pyrolysis.

Introduction

The intensity of research in the U. S. and abroad into the liquefaction of coal has largely been directed toward reduction of the demands on petroleum feedstocks. Both traditional fossil fuel feedstocks and alternative feeds are rich in sulfur and nitrogen, and removal of these heteroatoms has therefore been studied in detail. Oxygen removal is less well studied although large quantities of oxygen are found in biomass and coals. Herein we focus attention on the former feed.

Wood comprises cellulose, hemicellulose and lignin portions, with proportions of the latter typically one-third by weight. The potential for upgrading lignin to useful chemicals or fuel additives has been demonstrated [5]. Moreover, the structural elements of lignin are well enough understood to make it an attractive substrate for study. The study of lignin thus provides an opportunity for generalization about the reactions of lignites and low-rank coals that share similar structural features.

Lignin pyrolysis is to rather low yields of useful single-ring phenolics (10-15%), and as many as 33 different phenolics form, each in low yield, rather than any one in a usefully high yield [1,3,7,8,9,10]. Much of the original lignin weight is lost to a high molecular weight char, suggested by model compound experiments to form via a polymerization of ortho oxygen-containing guaiacyl moieties characteristic of lignin [11]. Petrocelli [16] has suggested that the catalytic hydrodeoxygenation (HDO) of lignin should reduce char formation by removing some of the guaiacyl oxygen as water and thus circumventing the polymerization to char; the single-ring phenolic fraction is also substantially simplified as a result.

This motivated the development of a model compound based and thus predictive computer simulation of lignin liquefaction. This would allow scrutiny of the feasibility of various lignin upgrading schemes by testing various processing strategies in a quantitative link of the competing factors of reaction, diffusion, catalyst deactivation, substituent effects and multiple bond identities.

A stochastic model of depolymerization has several advantages over deterministic models. First, substrate heterogeneities, including substituent effects, multiple linkage types, and an unusual molecular weight distribution are easily addressed in a stochastic model. Second, a Monte Carlo model can account for the molecular weight of each reactive moiety separately, which facilitates proper modeling of the diffusion and reaction in a porous catalyst. Thus, the classic approximation of equal reactivity need not be invoked. Finally, the processes involved in chemical kinetics may well be stochastic, so it seems reasonable to model them as such.

Background and Model Development

Stochastic Kinetics

The stochastic approach to chemical kinetics is well known [14] and has been applied by McDermott [13] and Squire [19] to model the decomposition of a simplified lignin polymer and coal, respectively. In one approach, the stochastic simulation of the polymer decomposition begins by dividing the total reaction time into small time steps of equal duration, after the passage of which the reactions of the polymer bonds are tested by comparing a characteristic reaction probability to a random number. Reaction occurs when this transition probability is greater than the drawn random number. In this manner, each bond along the polymer chain is tested for reaction, and the procedure is repeated through time in increments of Δt until the desired final time is reached. This process is equivalent to mapping out a first-order Markov chain through time, as illustrated in Figure 1, where the new physical state of the system depends solely on the previous state of the polymer. The Monte Carlo simulation is the average result of a large number of Markov chains.

The transition probability for the first-order reaction of A to B follows the Poisson distribution and has the general form shown in Equation 1:

$$P_{AB} = 1 - e^{-k_{AB}\Delta t} \tag{1}$$

Thus both the size of the time step and the overall rate constant dictate the likelihood of reaction. For the present model of the catalytic liquefaction of lignin, the appropriate k_{AB} for a given moiety included factors for diffusion limitations and catalyst age. Thus, the transition probability for each reactive moiety in lignin had a catalytic and thermal component, as in Equation 2:

$$P = 1 - e^{-(\eta \Phi w_c k_c + k_t)\Delta t} \tag{2}$$

where η = catalytic effectiveness factor; Φ = catalyst activity; k_c = intrinsic catalytic reaction rate constant, $l/g_c \cdot s$; w_c = catalyst bed loading, g_c/l; Δt = reaction time step, s; k_t = intrinsic thermal reaction rate constant, s^{-1}.

Lignin Structure

The lignin reactant was assembled randomly. This was accomplished by transferring the detailed information contained in chemical models for lignin structure [4,18] into probabilities of substituent and bond types present on each position of an average aromatic ring as illustrated in Figure 2. Four ring positions were required to define a lignin ring, and two of these identified as P1 and P2 contained primarily oxygen-bearing substituents and linkages, whereas the other two identified as H1 and H2 contained hydrocarbon substituents. Coupling this substituent distribution information with the details of the initial distribution of lignin molecular weights allowed random generation of linear lignin polymers of appropriate lengths.

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In practice, a drawn random number was placed onto the integral probability distribution of substituent and linkage types at each of the four ring positions. This assembly determined each substituent and linkage type along a lignin polymer chain whose length was determined by placing a drawn random number on the integral molecular weight probability distribution. Repetition according to the Monte Carlo technique allowed generation of an appropriate starting lignin.

Lignin Reactions

The reaction pathways and intrinsic kinetics parameters were deduced from related model compound experiments reported elsewhere [6,8,11,12,13,15,16,20]. The operative reaction pathways and kinetics parameters elucidated are summarized in Table 1.

Catalyst Deactivation

Model compound reactions in a flow microreactor allowed observation of the decay of catalyst activity with time on stream. This is illustrated in Figure 3 for the reaction of 2-hydroxydiphenyl-methane at 2250 psig H_2, 250°C and WHSV=0.49 hr^{-1} [20]. Best fit models relating the observed activity losses to the quantity of oxygen-containing species lost (C_c) to char were of the form

$$\Phi = e^{-\alpha C_c} \tag{3}$$

and

$$\Phi = \frac{1}{1 + \alpha C_c} \tag{4}$$

and associated deactivation parameters (α) are listed in Table 1.

Catalyst Effectiveness

The parallel events of diffusion and reaction of lignin oligomers in catalyst pores were modeled in terms of a catalyst effectiveness factor, which was a function of oligomer molecular weight and degree of polymerization (DP) as follows:

$$\eta = \frac{1}{\phi} \frac{3\phi \coth 3\phi - 1}{3\phi} \tag{5}$$

$$\phi = f(k_c, DP) \tag{6}$$

For relatively short lignin polymers (DP < 200), Rouse's model for coiling polymers in dilute solutions [17] dictated that the Thiele modulus ϕ be proportional to the square-root of DP. The diffusion of longer polymer chains (DP > 200) was modeled using de Gennes reptation theory, in which diffusion is inversely proportional to the square of molecular weight [2]. Under these conditions, and the Thiele modulus was proportional to DP.

Integration

Equations 3, 4 and 5 and the intrinsic model compound kinetics of Table 1 were integrated into a stochastic model of lignin depolymerization in terms of the transition probabilities of Equation 2. The resulting simulation was capable of predicting the product spectrum resulting from the thermal or catalytic depolymerization of kraft and milled-wood lignin.

Results and Discussion

Simulations of kraft lignin pyrolysis and catalytic liquefaction were at 380 and 400°C. The predicted product yields from catalytic liquefaction of kraft lignin at 380°C, 2250 psig and 2.47 g_{lignin}/g_c in a batch reactor (case 1) illustrated in Figure 4 increase with time to 0.23 and 0.17 for single-ring products and char, respectively after 30 min.

Figure 4 also illustrates the effects of catalyst deactivation and internal transport. Simulations run in which both were either included or neglected provided limiting cases. Intrinsic kinetics resulted in the highest yields of single-ring products and the lowest yield of char, whereas allowing for catalyst deactivation and diffusional limitations resulted in the lowest single-ring product yield and highest char yield.

The effects of polymer diffusion and catalyst deactivation were also considered separately. The remaining curves of Figure 4 illustrate. The diffusional limitation was largest initially, where polymer molecular weight was high, as both single-ring products and char evolved at lower rates initially than in the limiting case of no internal transport limitations. Moreover, inspection of the yields of these products after 30 min shows that transport had little effect on the ultimate evolution of single-ring products and char. Finally, the remaining curve in Figure 4 illustrates that the effect of catalyst deactivation was largest at longer reaction times, and lower ultimate yields of single-ring products were accompanied by greater quantities of char.

The more rapid catalytic liquefaction relative to thermal depolymerization is illustrated in Figure 5 as a plot of the number molecular weight distribution parametric in reaction time. For catalytic depolymerization, a 15% yield of single-ring products was realized after only 10 min at which time the thermal yield of single- ring products was only 4%.

The temporal variation of monomer and char yield for pyrolysis and catalysis are illustrated in Figure 6 along with a measure of the selectivity to char over single-ring products. The yields of single-ring products were greatly increased upon reaction over a catalyst compared to thermal treatment alone, and char formation was decreased by roughly half. This agrees with the experimental findings of Petrocelli [16] and Train [20] that single-ring product yields were roughly doubled compared with pyrolysis. Moreover, the selectivity to char decreased rapidly to roughly 0.5 with catalytic treatment compared with the steady increase predicted with pyrolysis.

The identities of the major products in the single-ring product fraction are shown in Figure 7 as a plot of product yield versus reaction time. Whereas products containing two oxygen substituents (guaiacols and catechols) accounted for nearly half of the monomeric products evolved from pyrolysis, yields of these products were only 5% of the single-ring products formed by catalytic liquefaction. As a result, yields of both phenols and hydrocarbons increased substantially with catalytic treatment.

Finally, the simulation predictions are compared with experimental kraft lignin pyrolysis [8,9] and catalytic liquefaction [20] results in terms of the products of the monomer fraction in Figure 8. The agreement between simulated and experimental kraft lignin pyrolysis at 400°C is quite favorable. The agreement between simulated and experimental catalytic liquefaction at 380°C is still qualitatively good but quantitatively poorer.

Conclusions

The Monte Carlo simulation is a convenient and flexible tool for predicting the depolymerization of macromolecular substrates. Not only intrinsic kinetics but also catalyst deactivation and diffusional limitations can be addressed. The simulation predictions herein were in good qualitative agreement with experimental results, and agreement between predicted and experimental proportions of hydrocarbons, phenols, guaiacols and catechols in the monomer fraction was excellent. The practical significance is the prediction that removal of at least one of the oxygen-containing substituents from phenolic rings by catalytic HDO should reduce char formation and simplify the resulting phenolic product spectrum.

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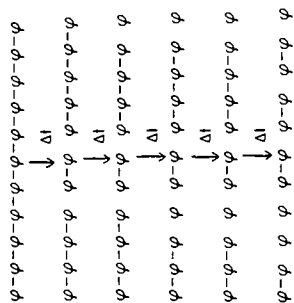[20] Train, P. M. PhD thesis, University of Delaware, 1986.

Figure 2: Cumulative probability distributions function for substituents on aromatic ring positions (a) H1, H2 and (b) P1, P2.

Figure 1: Random reaction trajectory of a polymer chain.

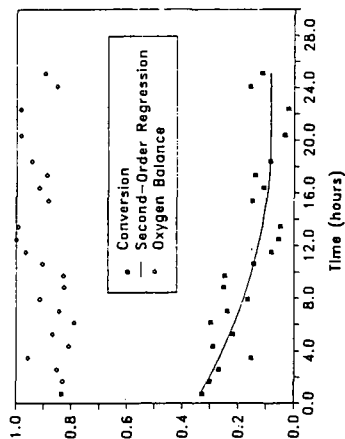**Figure 3:** Catalyst deactivation in the reaction of 2-hydroxydiphenylmethane over Co-Mo/γ-Al₂O₃ at 250° C, 2250 psig, WHSV=0.49 hr⁻¹
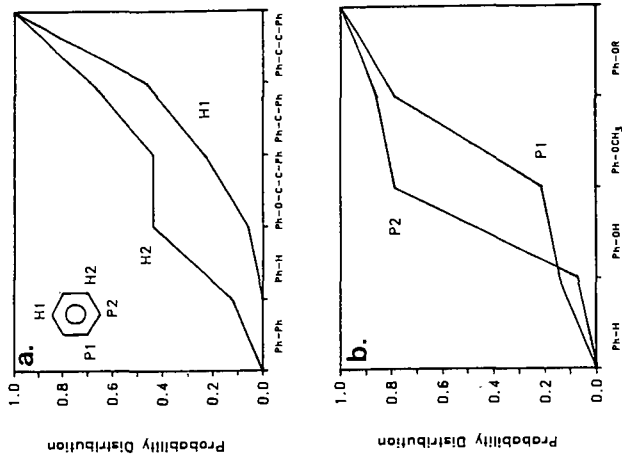
Conversion
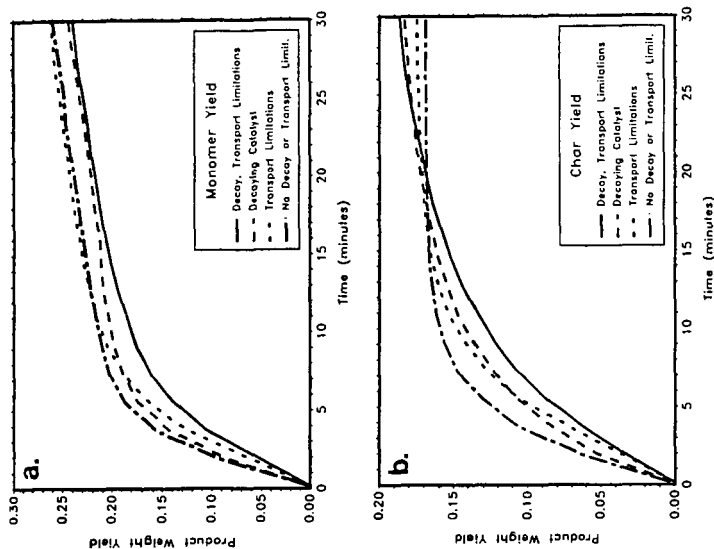Second-Order Regression
Oxygen Balance

Time (hours)

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Figure 4: Effects of catalyst deactivation and transport limitations on lignin depolymerization (case 1). (a) monomer yield (b) char yield.

a. **Monomer Yield**
Legend:
— Decay, Transport Limitations
– – Decaying Catalyst
· · · Transport Limitations
–·– No Decay or Transport Limit.

Product Weight Yield (0.00–0.30) vs Time (minutes) 0–30.

b. **Char Yield**
Legend:
— Decay, Transport Limitations
– – Decaying Catalyst
· · · Transport Limitations
–·– No Decay or Transport Limit.

Product Weight Yield (0.00–0.20) vs Time (minutes) 0–30.

Table 1: Summary of model compound kinetic and reaction pathways.

Reactant	Primary Products	Thermal Parameters log A (s-1)	E (kcal/mol)	Source	Catalytic Parameters log A (1/gc·s)	E (kcal/mol)	Source
Veratrole	Guaiacol / Anisole / Phenol	11.4 / 10.6 / 8.7	48 / 47.4 / 41.6	[1] [1] [1]	4.0 / - / -	21.7 / - / -	[28]
Guaiacol	Catechol / Phenol / Char	12.6 / 11.7 / 8.4	48.3 / 45.7 / 42.7	[1] [1] [1]	5.2 / 6.1 / 1.6	25.1 / 28.1 / 15.8	[18] [16] [16]
Catechol	Phenol / Char	4.9	25.2	[8]	6.8 / -0.5	29.3 / 16.6	[18] [16]
Anisole	Phenol / Benzene	9.1 / 17.2	42.2 / 60.7	[1] [1]	8.0 / 8.0	29.7	[5]
Phenol	Benzene				-1.9	6.7	[16]
Diphenylmethane	Toluene+Benzene	12.7	64.6	[16]	2.9	21.16	[28]
CHO	Phenol+Toluene / o-Cresol+Benzene	9.6	43.4	[11]	9.2 / 7.8	38.1 / 35.2	[18] [16]
Diphenylethane	2 Toluene / Ethylbenzene+Benzene	18.2 / 6.6	45.3 / 44.5	[16] [16]			
2-Phenylphenol	Phenol+Benzene	x			-2	8.2	[16]
o,o'-Biphenol	2 Phenol	x			$-\log_{10} A_{150} = 7.26$		[16]
PPE	Phenol+Ethylbenzene	11.1	45.0	[12]			
GGE	Guaiacol+AV	5	20.8	[13]			
Phenyl Ether	Phenol+Benzene	16.0	72.1	[11]	8.7	35.4	[18]
4-Phenoxyphenol	2 Phenol				8.7	32.2	[20]

CHO = 2-hydroxydiphenylmethane
PPE = Phenethyl Phenyl Ether
GGE = Guaiacylglycol-β-guaiacyl Ether
AV = Acetovanillone

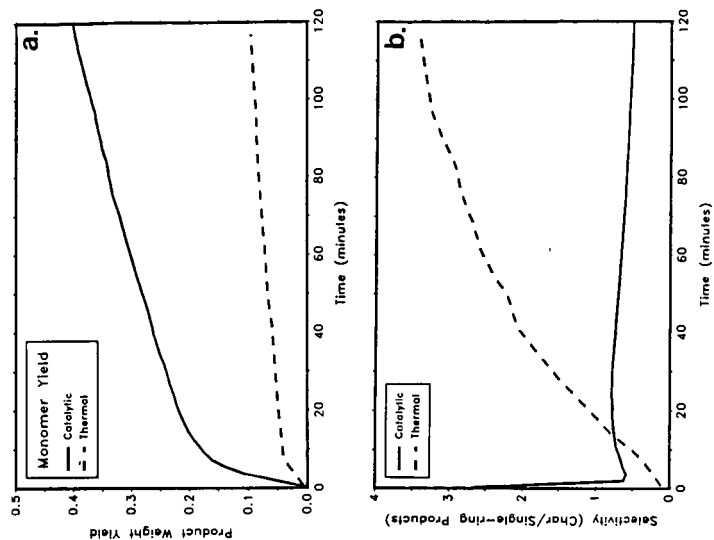| Deactivation Parameters [28]	Q (mol O/gc)	Form of Activity Function
Single-Ring Phenolics	589.2	Equation 4
Carbon Linkages	273.5	Equation 3
Ether Linkages	28.8	Equation 3

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Figure 6: Comparison of thermal and catalytic liquefaction strategies. (a) monomer yield (b) selectivity (char/monomer)
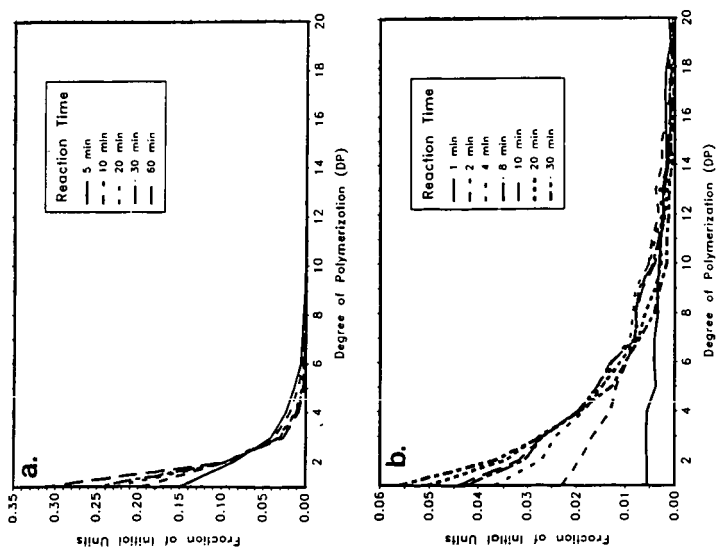

Figure 6: Temporal variation of the molecular weight distribution of a reacting lignin polymer. (a) catalytic (b) thermal
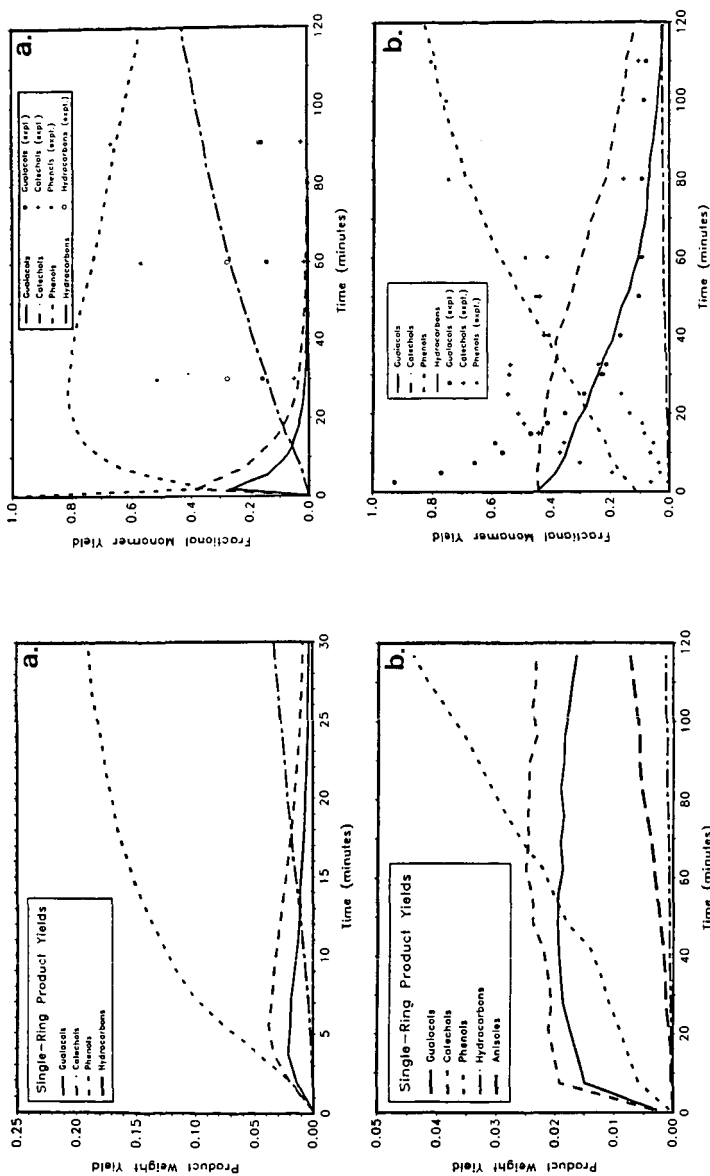
247

Figure 8: Comparison between simulation and experimental results. (a) catalytic (b) thermal

Figure 7: Comparison of single-ring product classes produced by thermal and catalytic liquefaction strategies. (a) catalytic (b) thermal

Catalytic Hydrodeoxygenation and Dealkylation
of a Lignin Model Compound

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ABSTRACT

A comparison is presented of the hydrotreatment of 4-propylguaiacol (4PG) exploring two catalysts: MoS_2 on γ-alumina and the dual functionality MoS_2/NiS on phosphated γ-alumina at 250°-450°C and 500 psig of hydrogen. The catalyst with acidic support was found to promote substantial dealkylation of 4PG into a number of alkylated phenols such as methyl- (predominantly meta- and para-), ethyl-, and methylpropyl-phenols. The main reaction product on the less acidic catalyst was 4-propylphenol. At 350°C, mild deoxygenation to phenols can be maximized, whereas higher temperatures favor the formation of hydrocarbons, aromatic and saturated. Higher space velocities also favor mild deoxygenation to phenols. These studies are relevant to the conversion of lignins into phenolic compounds. Transformation of phenols into methyl aryl ethers produces a suitable gasoline octane enhancer and extender.

INTRODUCTION

In the production of liquid fuels from lignocellulosic materials, the carbohydrate components can be converted into ethanol fuels in fermentation processes. However, the lignin fraction, composed of phenylpropane units, is not amenable to such a conversion, but can be transformed into phenolic compounds and hydrocarbons. The phenolic fraction, when converted into methyl aryl ethers, can be blended with gasoline, together with the hydrocarbon (primarily the aromatics) fraction. Singerman (1) demonstrated that methyl aryl ethers produced from coal liquids are fully compatible with gasoline to replace or supplement the aromatic components (e.g., benzene, toluene, xylenes). The most desirable phenols for conversion into methyl aryl ethers are phenol, cresols, and xylenols because the resultant ethers have high octane numbers and their boiling points fall within the range of gasoline. We are investigating the conversion of lignins into phenols and hydrocarbons (2) by mild hydrodeoxygenation (HDO) routes.

The approach taken is based on coal and petroleum hydrotreating processes as well as early work in the field of hydrodeoxygenation (HDO) of lignins (refs. 3-7), that has recently been reviewed (8). MoS_2 on γ-alumina catalyst was considered the best for the hydrocracking stage of the Hydrocarbon Research Institute's Lignol Process (9), in which hydrotreating was followed by thermal dealkylation for the production of phenol and benzene. An optimal catalyst for the conversion of lignins into phenols would possess the following characteristics: high conversion at modest temperatures to minimize char formation from lignin, high selectivity to phenols to prevent higher hydrogen consumption that accompanies hydrocarbon formation, dealkylation capability for side chain removal or rearrangement, tolerance to water formation, durability, and reasonable cost.

In order to select the best catalysts, well-defined lignin model compounds (e.g., 4-propylguaiacol, or 2-methoxy,4-propylphenol) containing representative function-alities have been employed. The aim is two-fold: mild deoxygenation into 4-propylphenol and partial dealkylation into methyl-, and ethyl-phenols. A commercial

catalyst and a custom-synthesized heterogeneous catalyst (10) have been screened for their HDO and dealkylation activities. The results reported here are preliminary but illustrate the utility of bi-functional HDO catalysts in lignin-model compound hydrodeoxygenation.

EXPERIMENTAL

Equipment. A trickle-bed reactor was constructed from 1/2-in. OD 316 stainless steel (SS) tubing with a 0.035-in. wall thickness and Swagelok tube fittings. The catalyst bed was supported by a 90 micron SS frit which in turn was supported by a 1/16-in. K type thermocouple. The thermocouple entered the reactor from the bottom through a Tee fitting (see Fig. 1). The reactor was suspended vertically in a Lindberg oven (Model 55035). The outlet lines were heat taped and nominally maintained at 160°C between the reactor and the high-pressure condenser. The condenser was constructed from a Whitey 150 mL SS sample cylinder to which copper tubing was silver soldered. During operation, the condenser was maintained at -5°C. The pressure letdown valve was a Whitey SS-22RS-4. A second condenser made from a 3-oz Fisher-Porter bottle was installed downstream of the letdown valve and was immersed in a Dewar filled with isopropanol/dry ice. The rest of the gas handling train consisted of a gas sampling port, Matheson rotameters for flow measurement, and a heavy walled flask containing saturated KOH for scrubbing H_2S before venting to the exhaust system. The parallel gas train which splits at the three-way ball valve, upstream of the letdown valve, allowed continuous operation during liquid sampling from the condenser (Fig. 1). The feed mixture was injected into the reactor by a calibrated Isco model LC-5000 high-pressure syringe pump. Hydrogen was supplied from a high-pressure cylinder with a regulator.

The trickle-bed reactor currently in use has been modified to improve mass balance and ensured adequate catalyst particle wetting and minimized liquid channeling. Thicker wall tubing has been employed in the reactor, and VCR glands were welded to both ends, adapted to a pipe threaded Conax fitting at the top and a 1/2 in. to 1/4 in. Swagelok reducer at the bottom. Directly below the reactor is a high-pressure condenser constructed from a Whitey SS sample cylinder of 150 mL volume. During operation the condenser is maintained at -5°C.

Materials. The catalysts used include $MoO_3/\gamma-Al_2O_3$ supplied by Strem Chemicals (#42-1500). The MoO_3 content was 10%-12%, and the surface area was 64 m^2/g in the form of 3/16 in. x 1/8 in. pellets. The pellets were ground with a mortar and pestle and sieved to 20-14 mesh before loading into the reactor. $Ni0/MoO_3$ on phosphoric acid co-precipitated γ-alumina was supplied by M. Maholland and S. Cowley at the Colorado School of Mines. Their detailed preparation and properties are described elsewhere (10). The Ni and Mo contents of the catalyst were 3% and 11.7%, respectively. The P:Al atomic ratio was 0.5, surface area was 8.2 m^2/g, and the average pore diameter was 210 Å. The catalysts were presulfided in-situ by injecting a solution of 5 vol % methyldisulfide in hexane in the presence of hydrogen at 100 psig. The liquid and gas flow rates were calibrated to maintain approximately 10 vol % H_2S in hydrogen. The presulfiding was performed at 200°C for two hours then 400°C for and additional two hours.

Research grade hydrogen (99.999%) was used as supplied. 4PG was used without further purification as supplied by Frinton Laboratories (#1035). The feed mixture was 75 vol % 4PG in research grade hexanes with 0.25 vol % methyldisulfide (Aldrich #15,031-2) to maintain catalyst sulfidation. Burdick and Jackson UV-grade acetonitrile was used as supplied to dilute the liquid samples prior to analysis.

<u>Analysis.</u> The liquid samples (generally 0.75-1 g) were diluted to 100 mL in acetonitrile.

Water Determination:
   The diluted samples were mixed 1:1 with an internal standard solution of absolute methanol in acetonitrile. The separation and quantitation of water was performed on a Varian 3700 gas chromatograph equipped with an autosampler, integrator, and a glass column 6 ft x 0.2 mm ID packed with Porapak QS. The carrier gas was high-purity helium.

Hydrocarbons and Phenolics Determination:
   The individual reaction products were identified on a Hewlett Packard Model 5985 GC/MS. Each identification was checked by search and comparison with computer library spectra and by comparison with mass spectra generated from known standards for most of the compounds. The components were also identified by their retention times and were quantified on the Varian 3700 using a Supelco SPB5 wide bore capillary column, 30 m x 0.75 mm ID, 1-μ film. The column temperature was programmed starting at 40°C, held for two minutes then increased at a rate of 3 degrees/minute to 280°C. The injector and flame ionization detector temperatures were 220°C and 280°C, respectively. Helium carrier gas was used at 12 mL/min.

Gas Analysis:
   Gas samples were analyzed on a Carle Model 111H gas chromatograph equipped with two thermal conductivity detectors, one for H_2 and the other for light hydrocarbons. After sample injection, hydrogen was separated by a Pd diffusion tube at 600°C and then a 5 ft x 1/8 in. Porapak Q (80/100) column using N_2 as the carrier gas. The remaining gases were separated on a series of three columns: (1) 6 ft x 1/8 in. Molecular Sieves, (2) 2.5 ft x 1/8 in. Squalane, and (3) 12 ft x 1/8 in. n-octane Poracil C using He as the carrier gas. The columns were accessed sequentially by automatic valves which are controlled by a Hewlett Packard 3388A integrator.

<u>Operating Procedure.</u> The reactor was operated in the integral mode for catalyst screening. The reactor was loaded with 1-1.5 g of catalyst which was presulfided as described above. A typical experiment was performed as follows. The chilled water circulator, oven, and heating tape were switched on and set to the desired temperatures. The hydrogen pressure regulator was used to pressurize the system to 500 psig. The syringe pump was loaded with the feed mixture and calibrated to the desired flow rate. Once all the temperatures had stabilized, the syringe pump was switched to inject the feed into the reactor and the hydrogen flow rate adjusted with the letdown valve to give the desired rate of 900 mL H_2/mL 4PG (equivalent to a typical petroleum hydrotreating rate of 5000 SCF/bbl). The system was allowed to equilibrate for one hour before sampling began. Liquid samples were obtained by switching to the parallel gas train, thereby isolating the condenser which was then depressurized. Samples were removed with a syringe through a septum at the bottom of the condenser. One gas sample was obtained toward the end of each run by switching to the parallel gas train, attaching an evacuated SS sample cylinder to the sampling port, and opening the letdown valve slightly to fill the cylinder.

Results and Discussion

4-Propylguaiacol has been hydrotreated under a variety of conditions using MoS_2/γ-Al_2O_3 and NiS-MoS_2/P:γ-Al_2O_3 catalysts in the temperature range of 250-450°C, at two molar hourly space velocities (MHSV 0.007 and 0.017 moles 4PG/g cat.*h which correspond to WHSV = 1.17 and 2.82 g 4PG/g cat.*h, respectively). Based on early

experiments to determine the effect of hydrogen pressure on the reaction, we found that decreasing the pressure from 1000 psig to 500 psig increased the selectivity of propylphenol formation 89% with no significant effect on the overall conversion using the MoS_2 catalyst. Therefore, all experiments reported here were performed at 500 psig.

The major phenolic product from the $MoS_2/\gamma-Al_2O_3$ catalyst was 4-propylphenol having a maximum selectivity of 47% at $350^\circ C$ and MHSV = 0.007 (see Table 1). At higher temperatures, hydrocarbon products such as propylbenzene, methylpropylbenzenes and propylcyclohexane are predominant. No reaction conditions studied so far with this catalyst have given significant yields of dealkylated products. This result is not surprising given that $\gamma-Al_2O_3$ is not a very acidic support.

Table 1.   Selectivities of Major Products on $MoS_2/\gamma-Al_2O_3$

Temp. (°C)	Conversion (%)	Propylphenols (%)	Propylbenzenes (%)	Propylcyclohexane (%)
250	38	7.3	2.9	0
300	36	35.7	8.7	0
350	82	48.5	8.5	1.3
400	95	11.1	14.6	4.0
450	99	5.9	25.5	5.5

All reactions run at 500 psig, MHSV = 0.007 moles 4PG/g cat.*h. Conversion = (moles $4PG_{in}$ - moles $4PG_{out}$)/moles $4PG_{in}$ * 100. Selectivity = moles product/moles 4PG converted * 100.

The product slate obtained from 4PG on the $NiS-MoS_2/P:\gamma-Al_2O_3$ catalyst is notably different from that of the $MoS_2/\gamma-Al_2O_3$ catalyst. 4-Propylphenol remained the major product up to $350^\circ C$; however, significant dealkylation to phenol, cresols, and ethylphenols occurred (see Table 2). Figures 2 and 3 compare the selectivities of dealkylated phenolics from the two catalysts used. The more acidic catalyst support gave higher yields of dealkylated phenols at $300^\circ C$ than the neutral support did at $450^\circ C$ (6% vs. 3.5%, compare experiments 11 and 16 in Figures 3 and 2, respectively). This selectivity toward dealkylated phenols increased by a factor of 5 at $350^\circ C$ (compare experiments 15 and 16). Interestingly, GC/MS data suggests that the major cresols formed are meta- and para-cresol having a selectivity as high as 15.5% at T = $400^\circ-450^\circ C$ and MHSV = 0.017 moles 4PG/g cat.*h. Again, at higher temperatures the yields of phenols decrease at the expense of hydrocarbon production. This product shift can be offset by increasing the space velocity as demonstrated in Figure 4. At $450^\circ C$ and MHSV = 0.017, the selectivity to phenols is about 4 times the selectivity at MHSV = 0.007 (compare experiments 19 and 20 in Figure 4).

The gas analyses from the NiS/MoS_2 on phosphated γ-alumina catalyzed reactions support the evidence from the liquid analyses that the more acidic catalyst increases side chain cracking. At $400^\circ C$ only 0.2 mole % of propane was detected in the gas from the $Mo/\gamma-Al_2O_3$ catalyst, whereas using the more acidic catalyst support, 0.5 mole % of propane was formed plus from 0.1 to 0.5 mole % propene depending on the reaction temperature and space velocity. Water formation increased with increasing reaction temperature and followed the decrease in phenols selectivity above $350^\circ C$ because of hydrocarbon formation.

Table 2. Selectivities of Major Products on NiS–MoS$_2$/P:γ–Al$_2$O$_3$

Temp. (°C)	Conversion (%)	Propylphenols (%)	Ethylphenols (%)	Cresols (%)	Phenol (%)
300	53	32.2	1.8	4.0	0
350	63	48.1	9.8	16.2	4.4
400	96	4.4	5.6	13.3	7.0
450	100	0.7	1.7	4.4	4.4

All reactions run at 500 psig, MHSV = 0.007·moles 4PG/g cat.*h. Conversion and selectivity as defined in Table 1.

The results reported here, while preliminary, demonstrate the direction of our research efforts to test systematically, well characterized catalysts and develop, with researchers at the Colorado School of Mines, bi-functional catalysts for lignin hydrotreating. The data show that increasing the acidity of the catalyst support significantly increases the selectivity to dealkylated products. Additional catalysts with controlled acidity are under investigation to confirm the product trends described above. Complementing the model compound study, lignin investigations using a 300 mL stirred Autoclave Engineers high-pressure reaction vessel, operated in the semicontinuous mode are underway (11).
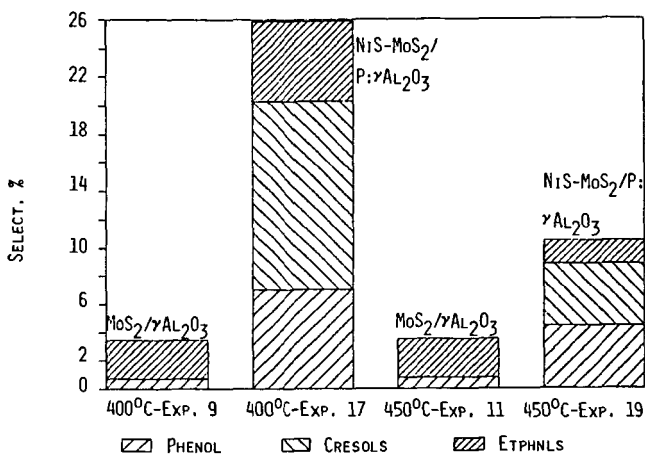
FIGURE 3. COMPARISON OF DEALKYLATED PHENOLS FROM 4-PROPYLGUAIACOL HYDRO-
TREATED ON MoS$_2$/γAL$_2$O$_3$ AND NiS-MoS$_2$/PHOSPHATED-γAL$_2$O$_3$. MHSV =
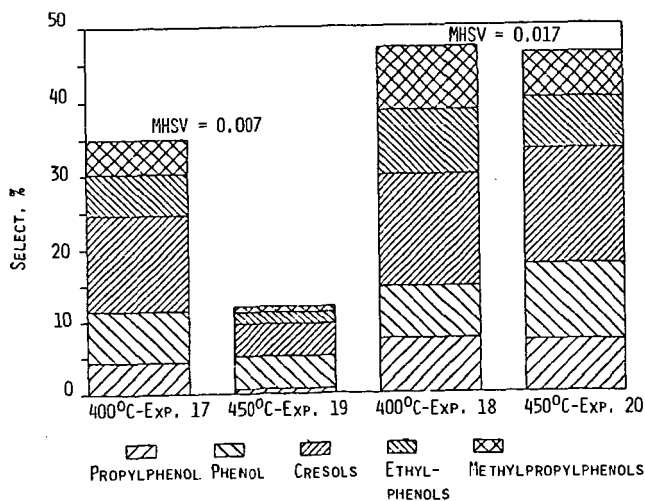0.007 MOLES 4PG/G CAT.•H.

FIGURE 4. EFFECT OF SPACE VELOCITY AND TEMPERATURE ON THE SELECTIVITY OF PHENOLS
FROM 4-PROPYLGUAIACOL HYDROTREATED ON NiS-MoS$_2$/PHOSPHATED γ-AL$_2$O$_3$.
MHSV = MOLES 4PG/G CAT.•H.

CATALYTIC HYDROTREATING OF BIOMASS-DERIVED OILS

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INTRODUCTION

Pacific Northwest Laboratory (PNL) is investigating the catalytic upgrading of biomass-derived oils to liquid hydrocarbon fuels. Tests have been conducted in a 1-liter, continuous feed, fixed-bed catalytic reactor at 250-450°C and 2,000 psig. This is envisioned as the second stage in a two-stage process to produce hydrocarbon fuels from biomass. Given that biomass can be converted to a liquid product, widely reported as phenolic (1-4), then oxygen removal and molecular weight reduction are necessary to produce usable hydrocarbon fuels. Upgrading biomass derived oils differs from processing petroleum fractions or coal liquids because of the importance of deoxygenation. This topic has received only limited attention in the literature (5-9).

HYDROTREATING BIOMASS-DERIVED OILS

Two types of biomass-derived oils have been studied at PNL. The first type of oil is produced by high pressure liquefaction at relatively long residence times. Oils identified as TR7 and TR12 in Table 1 were produced by this type of process at the Albany, Oregon Biomass Liquefaction Experimental Facility. These highly viscous oils consist primarily of substituted phenols and naphthols. The other type of oil is produced by low pressure flash pyrolysis at somewhat higher temperature and very short residence times. These oils are highly oxygenated and contain a large fraction of dissolved water. Because of the soluble water these have a much lower viscosity. The flash pyrolysis oil produced at Georgia Tech is typical of this type of oil. The fourth oil shown in Table 1 was made at PNL by pretreating the Georgia Tech pyrolysis oil to produce an oil more similar to the high pressure oils. Details of the pretreating step are given by Elliott and Baker (10).

Figure 1 shows some model reactions that are typical of what is required to produce liquid hydrocarbon fuels from biomass-derived oils. The three compounds, 2-methyl-2-cyclopentene-one, 4-methyl guaiacol, and naphthol are typical components of biomass-derived oils. The single ring compounds are upgraded primarily by deoxygenation. Hydrogenation of the aromatic structure is not desirable if high octane gasoline is the intended product, but it may be necessary as part of the pathway to cracking multiple ring compounds. Previous studies showed CoMo, NiMo and in particular sulfided CoMo to be the most effective catalysts for this combination of reactions (6). The heavy fraction of biomass-derived oils is not as well characterized and the reaction mechanism for upgrading is unknown. Use of an acidic support (such as a zeolite) compared to alumina may be beneficial for upgrading the high molecular weight fraction.

TABLE 1. Feedstock Oils for Hydrotreating Tests

	TR7 As Fed	TR7 Dry	TR12 As Fed	TR12 Dry	Georgia Tech Pyrolysis Oil As Fed	Georgia Tech Pyrolysis Oil Dry	Treated Georgia Tech Pyrolysis Oil As Fed	Treated Georgia Tech Pyrolysis Oil Dry
Elemental Analysis, wt %								
Carbon	74.8	77.5	72.6	76.5	39.5	55.8	61.6	71.6
Hydrogen	8.0	7.9	8.0	7.8	7.5	6.1	7.6	7.1
Oxygen	16.6	14.1	16.3	12.5	52.6	37.9	30.8	21.1
Nitrogen	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ash	0.5	0.5	3.0	3.0	0.2	0.3	0.0	0.0
Moisture	3.5	0.0	5.1	0.0	29.0	0.0	14.1	0.0
Density, g/ml @ 55°C	1.10	--	1.09	--	1.23	--	1.14[a]	
Viscosity, cps, @ 60°C	3,000	--	17,000	--	10[c]	--	14,200	
Carbon Residue, wt%[b]	13.5	13.9	26.9	28.3	--	27-31[c]	--	

a) at 20°C
b) TGA simulated Conradson carbon, see reference 12
c) Viscosity and carbon residue were measured for other similar pyrolysis oils

EXPERIMENTAL

The reactor system used for this study is a nominal 1-liter, continuous feed, fixed-bed reactor operated in an upflow mode. It has been described in detail previously (10,11). Operation in the downflow mode (trickle-bed) plugged the outlet line of the reactor with coke-like material and tests in this mode were discontinued. The oil feedstock, preheated to 40-80°C, is pumped by a high-pressure metering pump. Hydrogen from a high-pressure cylinder is metered through a high-pressure rotameter into the oil feed line prior to entering the reactor vessel. The reactor is 7.5 cm I.D. by 25 cm and holds approximately 900 ml of catalyst.

A two phase flow pattern exists in the reactor. Gas and volatile products move through the reactor quite rapidly. Unconverted, non-volatile material does not leave the reactor until it reaches the top of the liquid level and overflows into the product line. Pressure in the system is maintained by a Grove back-pressure regulator. Liquid product is recovered in a condenser/separator and the offgas is metered and analyzed before it is vented.

Catalysts used in the most recent hydrotreating tests are shown in Table 2. The Harshaw catalysts are conventional extruded CoMo and NiMo hydrotreating catalysts. The Haldor Topsoe catalysts are a composite system using low activity rings in the bottom of the bed to prevent plugging from carbon and metals, and high activity extrudates in the top of the bed. The last two catalysts are specialty catalysts incorporating a zeolite in the base to provide more acidity and promote cracking reactions.

TABLE 2. Catalysts Used for Hydrotreating Tests

Supplier Catalyst ID	Harshaw HT-400	Harshaw HT-500	Haldor Topsoe[b] TK-710	 TK-750	 TK-770	PNL/ Union Carbide CoMo/Y	Amoco NiMo/Y
Active metals, wt%	3% CoO 15% MoO$_3$	3.5% NiO 15.5% MoO$_3$	2% CoO 6% MoO$_3$	2.3% CoO 10% MoO$_3$	3.4% CoO 14% MoO$_3$	3.5% CoO 13.9% MoO$_3$	3.5% NiO 18% MoO$_3$ 2.5% P$_2$O$_5$
Support	Al$_2$O$_3$	Al$_2$O$_3$	Al$_2$O$_3$	Al$_2$O$_3$	Al$_2$O$_3$	Y-zeolite/ Al$_2$O$_3$	Y-zeolite/ Al$_2$O$_3$
Form[a]	1/8-in E	1/8-in E	3/16-in R	3/16-in R	1/16-in E	1/16-in E	1/16-in E

a) E - Extrudate, R- Rings, size given is O.D.
b) All three catalysts used in a layered bed

RESULTS AND DISCUSSION

The following discussion deals primarily with recent tests with TR12 oil and CoMo catalysts. Results of previous tests with other oils and catalysts will be summarized as they relate to the most recent efforts.

Tests with Cobalt-Moly Catalysts

Most of the test work has been done with the TR12 and TR7 oils and various sulfided CoMo catalysts. Table 3 shows results obtained with the TR12 oil and the Haldor Topsoe composite catalyst system at about 400°C, 2,000 psig and three different space velocities. Typically, the liquid product yield from the TR12 oil is about 0.9 1/1 of oil fed. At the low space velocity (0.11) the oil is 96% deoxygenated and is about one-third high quality aromatic gasoline (C$_5$ - 225°C). At even lower space velocities (~0.05) a liquid product containing about 60% gasoline and almost no oxygen can be produced. At higher space velocities (up to 0.44) deoxygenation is still good, nearly

TABLE 3. Results of Hydrotreating TR12 Oil with Haldor Topsoe Composite Catalyst

Run No.	HT-34	HT-34	HT-34
Temperature, °C	397	395	403
Pressure, psig	2,020	2,015	2,030
Space Velocity, LHSV, hr^{-1}	.11	.30	.44
Hydrogen Consumption, 1/1 oil fed	548	296	212
Product Yield, 1/1 oil fed	.92	.88	.94
Deoxygenation, wt%	96	87	79
Product Inspections			
Oxygen, wt%	0.8	2.5	3.8
H/C ratio, mole/mole	1.5	1.3	1.3
Density, kg/l	0.91	1.0	1.03
Yield C$_5$ - 225°C, LV%	37	24	11

80%, but hydrogen consumption decreases 50% or more resulting in a lower H/C ratio, higher density, and lower gasoline yield. The theoretical hydrogen requirement to deoxygenate TR12 is about 200 1/1 of oil. This indicates that at the low space velocity 350 1 H_2/1 oil is being used for hydrogenation, hydrocracking and other reactions. At the highest space velocity only about 50 1 H_2/1 oil is being used by these other reactions.

Table 4 shows results from hydrotreating TR7 with Harshaw CoMo/Al_2O_3 catalyst. Tests with the Harshaw catalyst and TR12 oil were similar to those with the Haldor Topsoe composite catalyst indicating the differences between Tables 3 and 4 are due primarily to the oil. At similar processing conditions, the products from TR7 are higher quality than those obtained from TR12. Analysis of TR7 and TR12 oils indicates TR7 is primarily single ring phenolics which when deoxygenated become gasoline boiling range aromatics. The TR12 oil is primarily double ring phenolics which require additional cracking and hydrogenation to produce light distillates.

When the Georgia Tech pyrolysis oil was hydrotreated with a sulfided CoMo catalyst at conditions similar to those used with TR7 and TR12 the runs had to be terminated due to severe coking in the bed. The temperature had to be reduced to 250°-270°C to prevent coking. The properties of the oil produced at these low temperatures are shown in Table 1 under the heading of treated Georgia Tech pyrolysis oil. This oil was further hydrotreated at 350°C and 2,000 psig with a sulfided CoMo catalyst and the results were similar to those obtained with TR7 and TR12. This is the basis for a proposed two stage upgrading process for biomass pyrolysis oils (10).

Results to date indicate 400°C is about the optimum temperature for hydrotreating biomass-derived oils. At 350°C a much poorer quality oil is produced. At 450°C the product quality improves somewhat compared to 400°C but the yield is reduced due to increased gas production.

TABLE 4. Results of Hydrotreating TR7 Oil with Harshaw CoMo/Al_2O_3*

Run. No.	HT-15	HT-14	HT-14
Temperature, °C	398	394	389
Pressure, psig	2,003	2,021	2,026
Space Velocity, LHSV, hr^{-1}	0.10	0.30	0.55
Hydrogen Consumption, 1/1 oil fed	616	435	202
Product Yield, 1/1 oil fed	0.99	1.0	0.88
Deoxygenation, wt%	~100	94	88
Product Inspections			
Oxygen	0.0	1.1	2.6
H/C ratio, mole/mole	1.65	1.41	1.32
Density, kg/l	0.84	0.91	0.96
Yield C_5-225°C, LV%	>87	60	28

* adapted from reference 11

Other Catalysts

In early tests with the TR7 oil where gasoline boiling range material was the primary product, the CoMo catalysts were preferred over NiMo because they retained the aromatic character and antiknock properties of the product. The NiMo catalysts were more active for hydrogenation and produced primarily saturated cyclic compounds (naphthenics) with a lower octane rating. With the TR12 oil a more active hydrogenation catalyst such as NiMo may be beneficial. Adding a cracking component such as y-zeolite to the catalyst may also be advantageous with the TR12 oil. Preliminary tests with a NiMoP/y-zeolite/Al_2O_3 catalyst obtained from Amoco are promising in this regard.

Catalyst Deactivation

A 48-hour test run was recently completed with TR12 oil and the Haldor Topsoe catalyst to evaluate catalyst deactivation. Figure 2 shows the trend of deoxygenation and hydrogen consumption at an LHSV of 0.1. Hydrogen consumption and the H/C mole ratio (not shown) fell rapidly in the early stages of the test and then leveled off. Deoxygenation fell throughout the test.

Two causes of deactivation have been postulated. The initial deactivation is likely due to coking of the catalyst which we have shown in earlier tests occurs primarily in the first ten hours (11). The longer term deactivation is probably due to buildup of metals, primarily sodium, from the oil. The TR12 oil contains about 3% ash, mostly residual sodium catalyst from the liquefaction process.

CONCLUSIONS

A variety of biomass-derived oils have been upgraded by catalytic hydrotreating in a 1-liter reactor system. Specific conclusions from our studies are as follows:

- High yields of high quality gasoline (C_5 - 225°C boiling range) can be produced from biomass-derived oils, however, low space velocities (long residence times) are required. At high space velocities a low oxygen, highly aromatic crude oil is produced.

- Cracking and hydrogenation of the higher molecular weight components are the rate limiting steps in upgrading biomass-derived oils. Catalyst development should be directed at these reactions.

- The TR7 oil is superior to TR12 and both are much superior to pyrolysis oils as feedstocks for catalytic hydrotreating to produce hydrocarbon fuels.

- Pyrolysis oils can be upgraded by catalytic hydrotreating, however, a catalytic pretreatment step is required.

- Residual sodium catalyst needs to be removed from liquefaction products to prevent rapid catalyst fouling.

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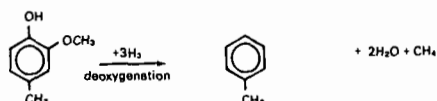
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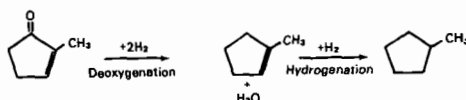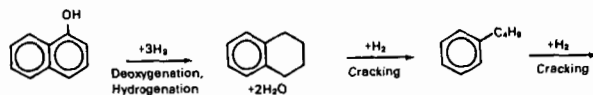
FIGURE 1. Some Reactions in Catalytic Hydrotreating Biomass-Derived Oils
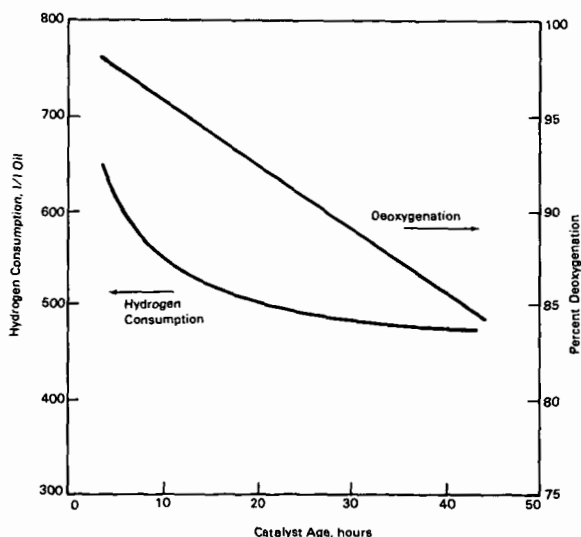

FIGURE 2. Effect of Catalyst Age on Deoxygenation and Hydrogenation, 400°C, 2,000 psig, LHSV = 0.1

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